Study of NiFe$_2$O$_4$ nanoparticles using Mössbauer spectroscopy with a high velocity resolution

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Abstract The nanocrystalline NiFe$_2$O$_4$ particles prepared by solution combustion synthesis technique using different fuels such as ethylene-diamine-tetra-acetic acid (NA sample) and urea (NB sample) were studied using magnetic measurement and ^{57}Fe Mössbauer spectroscopy with a high velocity resolution. The temperature dependence of magnetization is different for the two samples. Mössbauer spectra demonstrate the necessity to use more than two magnetic sextets, usually used to fit the NiFe$_2$O$_4$ nanoparticles spectra. Evaluation of the different local microenvironments for Fe in both tetrahedral (A) and octahedral (B) sites, caused by different Ni^{2+} occupation of octahedral sites, demonstrates at least five different local microenvironments for both A and B sites. Therefore, the Mössbauer spectra were fitted by using ten magnetic sextets which are related to the spread ^{57}Fe location in octahedral and tetrahedral sites.

Keywords Mössbauer spectroscopy with a high velocity resolution · Magnetic measurements · NiFe$_2$O$_4$ nanoparticles · Local microenvironments of the ^{57}Fe

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1 Introduction

It is well-known that among the spinel ferrites, $NiFe_2O_4$ nanoparticles applied in information storage, microwave devices, spintronics, magnetic resonance imaging, have been recently identified, as the suitable electrodes for Li-ion batteries and supercapacitors. $NiFe_2O_4$ has inverse spinel structure in which Ni^{2+} cations occupy octahedral (B) sites and Fe^{3+} cations occupy both B and tetrahedral (A) sites. It is well-known that cation distribution affects the physical, chemical and electrochemical properties of this material. Therefore, Mössbauer spectroscopy (MS) is a very useful tool for studying these materials. Previous studies of $NiFe_2O_4$ nanoparticles using MS demonstrated that the spectra consisted of two magnetic sextets with magnetic hyperfine fields around 500–550 kOe for the ^{57}Fe in B sites and 480–510 kOe for the ^{57}Fe in A sites [1–4]. The isomer shift of the ^{57}Fe in the B sites is larger than that in the A sites. Taking into account advances of MS with a high velocity resolution [5], we studied two different samples of $NiFe_2O_4$ nanoparticles, by using this MS technique combined with magnetic measurements.

2 Experimental

Samples of $NiFe_2O_4$ nanoparticles were synthesized by solution combustion synthesis technique using 2.45 g of $Ni(NO)_2·6H_2O$, 6.89 g of $Fe(NO)_3·9H_2O$ and 2.49 g of EDTA ($C_{10}H_{16}N_2O_8$). EDTA was used as fuel and the oxidant/fuel ratio was maintained as 1. The precursors were dissolved in double distilled water and the pH was adjusted to 7 by an addition of ammonia solution. The solution was heated on hot plate. Initially, the temperature was maintained below 100 °C for dehydrate the solution. After that, the temperature was suddenly increased up to 300 °C and an auto-ignition took place with evolution of gases. The collected samples were calcinated at 800 °C for 5 h. The same synthesis procedure was repeated with urea (CH_4N_2O) instead of EDTA. The $NiFe_2O_4$ particles were prepared by different fuels such as EDTA and urea are named as NA and NB, respectively.

These samples were characterized by X-ray diffraction (XRD) using Powder X-ray diffractometer PANalytical X'pert PRO with CuK_α radiation, scanning electron microscopy (SEM) using Quanta 200 with energy dispersion spectroscopy (EDS) and transmission electron microscopy (TEM) using JEM 2011. Magnetic measurements were carried out using commercial SQUID magnetometer MPMS-5S (Quantum Design). Mössbauer spectra were measured in 4096 channels by using an automated precision Mössbauer spectrometric system, built on the base of the SM–2201 spectrometer, with a high velocity resolution. The detailed characteristics of equipment and the spectra fit are given elsewhere [5, 6].

3 Results and discussion

XRD patterns of the NA and NB samples are shown in Fig. 1a, b which demonstrate the high purity and the highly crystalline nature of spinel $NiFe_2O_4$. No extra peaks are observed, confirming the purity of the samples. SEM and TEM images of the NB sample are shown in Fig. 1c, d. Chemical analysis of these samples carried out
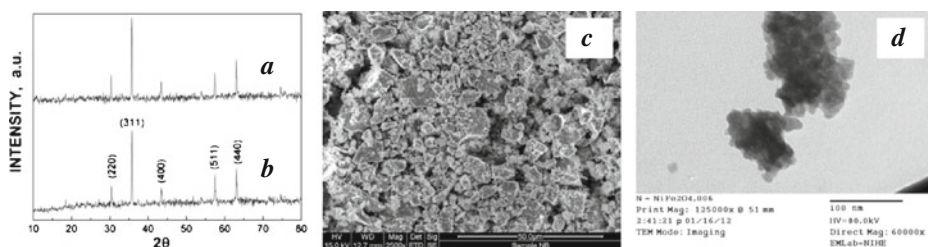
Fig. 1 X-ray diffraction patterns of the NB (**a**) and NA (**b**) samples, SEM (**c**) and TEM (**d**) images of the NB sample
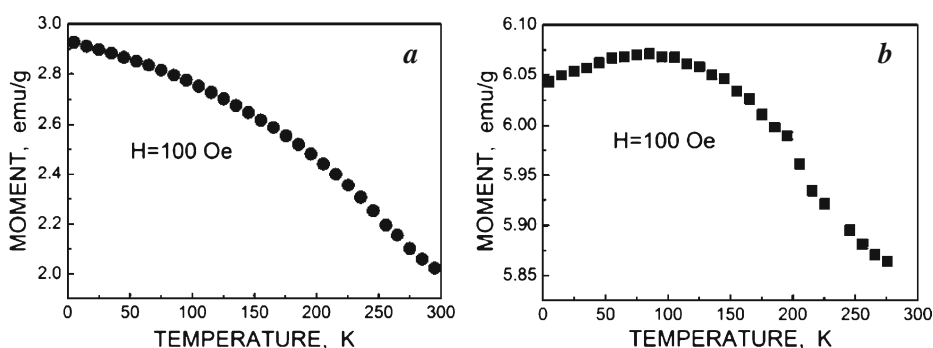

**Fig. 2** Temperature dependences of magnetization for the NA (**a**) and NB (**b**) samples

using EDS showed the following average composition: O—42 at.%, Fe—39 at.%, Ni—19 at.% for the NA sample and O—37 at.%, Fe—43 at.%, Ni—20 at.% for the NB sample. The nanoparticles sizes are 10–20 nm and 20–40 nm for NA and NB respectively.

The temperature dependence of magnetization of NA and NB samples appears to be different although measured under the same conditions (Fig. 2). For NA the gradual decrease of the moment with temperature is readily observed. Whereas for NB, first the magnetization increases up to ~100 K and then decreases with temperature. This difference may be a result of different nanoparticles size and shape magnetic anisotropy, and more studies are needed to clarify its source.

Mössbauer spectra of the NA and NB samples are shown in Fig. 3. These spectra look like spectra of similar compounds and visually consist of two sextets. However, the fit using two sextets was not good (see differential spectra for utmost sextet peaks from the NA spectrum fit using two sextets and inserted in Fig. 3a) and showed the necessity of more components. Therefore, we evaluated the probabilities of various Ni^{2+} numbers in the local environment of the A and B sites of the NiFe$_2$O$_4$ unit cell, within the spheres with a radius of 3.5 Å for both samples. Histograms of the calculated probabilities are shown in Fig. 4. On the basis of calculated probabilities ($\geq$0.05) we take into account at least 5 magnetic sextets for each A and B sites. The results of the spectra fit using 10 sextets are shown in Fig. 3. It is clearly seen much better differential spectra in both fits. The obtained Mössbauer parameters were grouped on the basis of the values of δ and H$_{eff}$. Five sextets with H$_{eff}$ in the
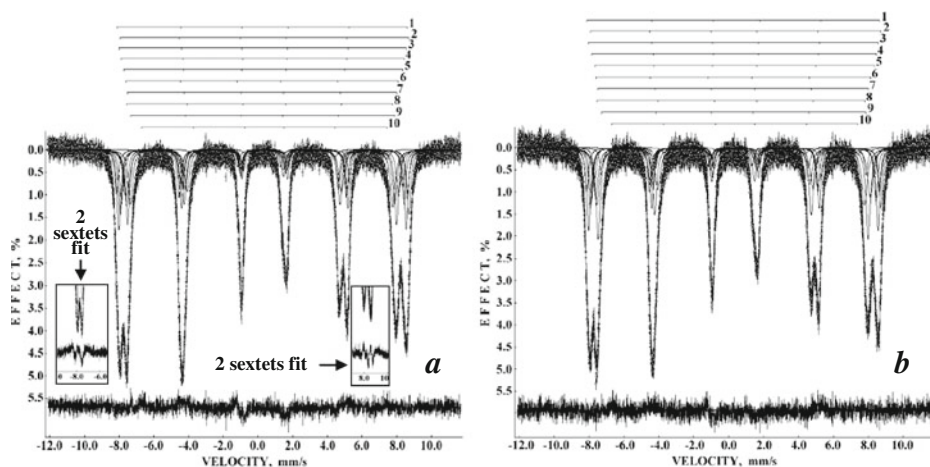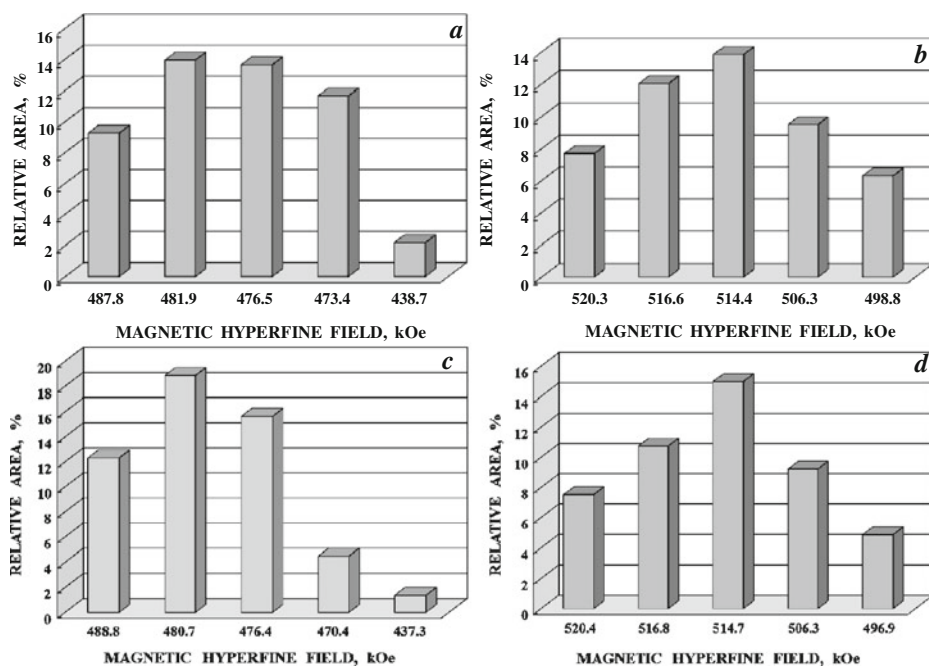
Fig. 3 Mössbauer spectra of the NA (**a**) and NB (**b**) samples measured in 4096 channels at T = 295 K. 1–10 are the components obtained by the appropriate fit. The differential spectra are shown below
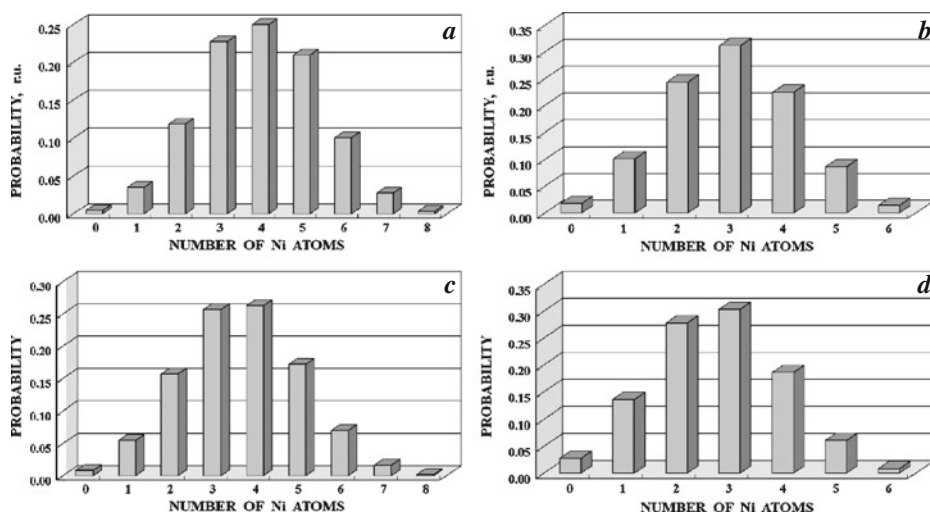
Fig. 4 Histograms of probabilities of various numbers of Ni^{2+} in local microenvironment of the ^{57}Fe in the tetrahedral (**a**, **c**) and octahedral (**b**, **d**) sites within the sphere of 3.5 Å radius in $NiFe_2O_4$ nanoparticles: the NA (**a**, **b**) and NB (**c**, **d**) samples

range of 499–520 kOe and δ in the range of 0.336–0.342 mm/s were related to the ^{57}Fe in the B sites while four sextets with H_{eff} in the range of 473–488 kOe and δ in the range of 0.163–0.258 mm/s were related to the ^{57}Fe in the A sites (this is in agreement with usual model fits [1–4]). The tenth sextet with $H_{eff} = {\sim}439$ kOe and $\delta = 0.371$ mm/s (S = ~2%) was also related to the ^{57}Fe in the A sites in spite of a larger value of δ (this may be a result of the effect of environment). If we propose that adding of one Ni^{2+} cation in the local microenvironment will reduce the magnetic

Fig. 5 Histograms of the relative areas of magnetic sextets related to the ^{57}Fe in the tetrahedral (**a**, **c**) and octahedral (**b**, **d**) sites for the fit of Mössbauer spectra of the NA (**a**, **b**) and NB (**c**, **d**) samples using ten magnetic sextets

hyperfine field on the ^{57}Fe, we can relate each sextet to the number of Ni^{2+} cations in the local microenvironment shown in Fig. 4. The histograms of relative areas of the components related to the A and B sites in both NA and NB samples are shown in Fig. 5. Thus, for the A site the largest value of H$_{eff}$ can be related to two Ni^{2+} cations while the smallest value of H$_{eff}$ can be related to six Ni^{2+} cations in the local microenvironment. In the case of the B sites the largest value of H$_{eff}$ can be related to one Ni^{2+} cation while the smallest value of H$_{eff}$ can be related to five Ni^{2+} cations in the local microenvironment. The total relative areas for the components related to the A and B sites were ~49% and ~51% and ~47% and ~53% for the NA and NB samples, respectively, which corresponds to samples stoichiometry.

4 Conclusion

Study of two different samples of NiFe$_2$O$_4$ nanoparticles using Mössbauer spectroscopy with a high velocity resolution demonstrated variations in ^{57}Fe microenvironments in both octahedral and tetrahedral sites, dependent on Ni^{2+} occupation numbers of octahedral sites. These variations were evaluated by calculations of different Ni^{2+} probabilities in the occupation of octahedral sites. Some variations in the Mössbauer parameters and different magnetization curves were obtained for the NA and NB samples. However, further investigations are required.

References

1. Šepelák, V., Bergmann, I., Feldhoff, A., Heitjans, P., Krumeich, F., Menzel, D., Litterst, F.J., Campbell, S.J., Becker, K.D.: J. Phys. Chem. C **111**, 5026 (2007)
2. Ramalho, M.A.F., Gama, L., Antonio, S.G., Paiva-Santos, C.O., Miola, E.J., Kiminami, R.H.G.A., Costa, A.C.F.M.: J. Mater. Sci. **42**, 3603 (2007)
3. Umare, S.S., Ningthoujam, R.S., Sharma, S.J., Shrivastava, S., Kurian, S., Gajbhiye, N.S.: Hyperfine Interact. **184**, 649 (2008)
4. Yu, B.Y., Kwak, S.-Y.: Dalton Trans. **40**, 9989 (2011)
5. Oshtrakh, M.I., Semionkin, V.A.: Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc. (2012). doi:10.1016/j.saa.2012.03.020
6. Semionkin, V.A., Oshtrakh, M.I., Milder, O.B., Novikov, E.G.: Bull. Rus. Acad. Sci. Phys. **74**, 416 (2010)